2nd. Edition

PATENT SPECIFICATION

568,009

Application Date: Nov. 24, 1942. No. 16628/42.
" " Nov. 24, 1942. No. 16631/42.
" " Jan. 22, 1943. No. 1149/43.

One Complete Specification left (under Section 16 of the Patents and Designs Acts, 1907 to 1942): March 18, 1943.

Specification Accepted: March 14, 1945.

PROVISIONAL SPECIFICATION
No. 16628 A.D. 1942.

Improvements in or relating to Toxicological Preparations

We, HARRY HURST and JACK HENRY SCHULMAN, both British Subjects, and both of Department of Colloid Science, The University, Cambridge, Cambridgeshire, and STAFFORD ALLEN AND SONS LIMITED, a British Company of Wharf Road, London, N.1, do hereby declare the nature of this invention to be as follows:—

The object of this invention is to provide toxicological preparations which are more efficient, for a given content of toxic agent, than the toxicological preparations at present available. By the term " toxic agent " we mean an insecticide, fungicide, bactericide or the like.

The penetration of many substances through artificial and natural membranes is greatly influenced by the nature of the particular " carrier " or " carriers," in which these substances are applied; in this respect artificial systems show many analogies to biological systems, and it is believed that the factors involved have hitherto been unrecognised.

For systems in which the toxic agent is capillary active, adjuvant action may depend on a number of different factors, e.g.

(a) The presence of water in a system may result in the production of high local concentrations of the toxic agent or agents in different component phases of the system. Water may change the phase distributions of the toxic agent or agents in such a way as to render them more readily available for toxic action in the particular biological system involved.

(b) Non-polar solvents such as kerosene may exert adjuvant action by changing the phase distributions of the toxic agent or agents in a particular system. More specifically, kerosene may facilitate the rate of entry of the toxic agent or agents into the biological systems in which kerosene may participate functionally.

(c) Further adjuvant action may take place in systems in which both (a) and (b) participate. More specifically water and a non-polar solvent may be present in the form of an emulsion. In such systems adjuvant action will depend on the gross summation of effects produced by

(1) Water
(2) Non-polar solvent
(3) The dispersion of relatively high concentrations of toxic agent or agents in the disperse phase.
(4) The production of high local concentrations of toxic agent or agents at the oil/water interfaces of the system.

For a toxic agent to be effective for a given purpose a certain threshold concentration is required. Where, for example, pyrethrins are supplied, in accordance with normal commercial practice, in the form of a solution in kerosene or heavier mineral oil, a certain definite quantity of pyerethrins per unit volume of solution is required for a given class of insect. Pyrethrins are very capillary active, and the concentration of pyrethrins at an oil/water interface is greater than the concentration in either of the bulk oil or water phases. If therefore the insecticidal preparation is presented to the insect in the form of an oil-in-water emulsion, a preparation containing a considerably smaller quantity of pyrethrins per unit volume of the preparation as a whole, than would be required in a kerosene solution of pyrethrins, will therefore be effective on the insect. There will be a further increase in the toxic effect owing to the relatively high concentration of the pyrethrins in the disperse phase, i.e. the oil.

Stated broadly, the invention provides a toxicological preparation, which comprises two liquids, one of them water and one of them dispersed within the other as an emulsion, a capillary active toxic

agent, an emulsifying agent, and a hygroscopic agent for preventing drying-off of the water and destruction of the interfaces on application of the preparation.

We prefer to use pyrethrins as the toxic agent and to use an emulsion of oil (e.g. kerosene) in water, and we find that glycerine, ethylene glycol and diethylene glycol are suitable hygroscopic agents. It is to be understood however that we may employ in place of oil other liquids which will form, in respect to water whether as the disperse or as the continuous phase, interfaces at which the toxic agent will be concentrated by adsorption.

As an alternative insecticide to pyrethrins, we may mention nicotine, Copper stearate and its derivatives are examples of fungicides which may be incorporated in toxicological preparations according to the invention.

It is preferred to employ as the emulsifying agent for producing an oil-in-water emulsion a mixture of water soluble emulsifying agent, such as sodium cetyl sulphate and an oil soluble emulsifying agent such as cholesterol. Such emulsifying agents produce an emulsion in which the disperse phase is negatively charged. An emulsion in which the disperse phase will be positively charged, can however be produced by using cetyl pyridinium bromide as the emulsifying agent.

It will be appreciated that the preparations according to the invention may be put on the market either in concentrated form, to be diluted before application, as for example by spraying, or alternatively in the dilute form, ready for application.

We are aware that preparations consisting of a kerosene solution of pyrethrins emulsified in water are known. It has not hitherto been realised, however, that it is possible to employ, in such preparations, a greatly reduced content of pyrethrins, for a given toxic effect, than is needed with a kerosene solution pure and simple. Nor has it been appreciated that the effectiveness of such an emulsion with a reduced pyrethrin content depends upon the preservation of the oil/water interfaces (and also of the water/air interfaces at which the pyrethrins may also be concentrated) during and after application by incorporation of a hygroscopic agent in the emulsion. Insecticidal preparations are usually applied, by spraying, in the form of a thin film and it will be understood that, unless a hygroscopic agent is included the oil/water and water/air interfaces will rapidly disappear owing to evaporation of the water.

The following laboratory data will show the greatly improved results achieved by using emulsions according to the invention in comparison with the results obtained using pyrethrins in kerosene solution. The signs + or − in the last column indicate respectively paralysis of the insects and failure to paralyse them under the conditions of the test. The two signs together indicate an indeterminate result.

	Pyrethrin content (weight per unit volume of liquid)	Knock down result
Kerosene	0.1%	+
	0.01%	±
	0.005%	−
	0.001%	−
Emulsion	0.1%	+
	0.01%	+
	0.001%	+
	0.0001%	±
	0.00001%	−

The following was the composition of the emulsion used in the above test:—

80% by volume of kerosene phase, containing 1% W/V (i.e. weight/volume) pyrethrins and 1% W/V cholesterol and 20% by volume of water phase containing 4% W/V sodium cetyl sulphate were made into an emulsion on a colloid mill, and diluted with 40 times its volume of water to give an emulsion containing about 0.02% pyrethrins. From 2 to 5% W/V of diethylene glycol was added to the dilute emulsion so obtained.

Dated this 24th day of November, 1942.

BREWER & SON,
Chartered Patent Agents,
28, Chancery Lane, London, W.C.2.

PROVISIONAL SPECIFICATION

No. 16631 A.D. 1942.

Improvements in or relating to Toxicological Preparations

We, Harry Hurst and Jack Henry Schulman, both British Subjects, and both of Department of Colloid Science, The University, Cambridge, Cambridgeshire, and Stafford Allen and Sons Limited, a British Company of Wharf Road, London, N.1, do hereby declare the nature of this invention to be as follows:—

The object of this invention is to pro-

vide toxicological preparations which are more efficient, for a given content of toxic agent, than the toxicological preparations at present available. By the term " toxic agent " we mean an insecticide, fungicide, bactericide or the like.

Walls and other surfaces are customarily treated, in order to free them from insects by the application to them of a thin film of a warehouse spray consisting of a solution of pyrethrins in a heavy oil. In practice the toxic effect disappears rapidly, owing to the passage of the pyrethrins into cracks and the like in the surface, and it is necessary to have recourse to repeated applications of the preparation in order to maintain a toxic film.

The invention is designed to avoid the difficulty by modifying the insecticides or other toxicological preparations at present in use in such a way as to immobilize the toxic agent, and prevent it from being rendered ineffective by passage into cracks or the like in the surface.

The invention accordingly provides a toxicological preparation, comprising a capillary active toxic agent, a liquid carrier for the toxic agent, and fine particles of dust in suspension in the liquid.

We prefer to use an oil, preferably a heavy oil of the medicinal paraffin type, as the carrier liquid, but we contemplate that volatile solvents may be used instead in suitable cases. The dust may be of any suitable inert material, e.g. silica, talc or calcium sulphate. The dust particles are conveniently first impregnated with the toxic agent (e.g. pyrethrins) and then suspended in the oil or other liquid to produce a preparation which can be applied as a spray.

The pyrethrins or other toxic agent are adsorbed at the surface of the dust particles and so immobilized and prevented from being lost by penetration into pores in the surface. Although the film produced by the application to the surface of a preparation according to the invention may be relatively non-toxic, a store of pyrethrins (o rther toxic agent) is nevertheless rendered available, and this can be utilized by the subsequent application to the film of water or some other hydrophilic agent. Water increases the mobility and hence the availability of the pyrethrins originally adsorbed at the surface of the dust; and the toxic effect of the film can be continuously resuscitated by repeated applications of water. We thus avoid the necessity for the further applications of toxicological preparation normally required.

A certain quantity of water is often present as an impurity on the surface of the dust particles, and this may in some cases be sufficient to render the film toxic. Where desired, however, a small quantity of water may be added to the suspension.

Where the carrier liquid is a volatile solvent, this will cause the dust to penetrate to some extent into the surface, and the toxic agent will, as explained above, be immobilized at the surfaces of the dust particles and available for use when the surface is afterwards wetted with water.

The toxic agent which is liberated by the water is however utilised to best advantage where oil is used as the carrier liquid, owing to the concentration of the toxic agent at the oil/water interfaces of the system as explained in our copending Application for Letters Patent No. 16628/42 of even date herewith.

Solid dust particles can sometimes aid in the emulsification necessary to form the oil/water interfaces, but this effect can be enhanced by incorporating in the preparation an emulsifying agent, preferably a mixture of oil-soluble emulsifying agent, such as cholesterol, and a water-soluble emulsifying agent such as sodium cetyl sulphate.

As an alternative to wetting the surface to be treated with water after application of the preparation for the purpose of obtaining water/oil interfaces in the film of preparation on the surface, water may be applied to the surface before it is treated with the preparation. As a further alternative a hygroscopic material, such as glycerine, may be incorporated in the suspension.

The suspension may, moreover, also include some convenient material for causing it to stick to walls and the like.

A suspension of a silica dust containing .5% by weight of pyrethrins in a heavy oil of the medicinal paraffin type, though relatively non-toxic in the absence of water, shows greatly increased toxicity when sprayed with a 1% solution of calcium chloride or in the presence of small quantities of water. The quantity of dust required per unit volume of oil to obtain the best results varies with the nature of the surface to be treated.

Dated this 24th day of November, 1942.
BREWER & SON,
Chartered Patent Agents,
28, Chancery Lane, London, W.C.2.

PROVISIONAL SPECIFICATION

No. 1149 A.D. 1943.

Improvements in or relating to Toxicological Preparations

We, STAFFORD ALLEN AND SONS LIMITED, a British Company, of Wharf Road, London, N.1, and HARRY HURST and JACK HENRY SCHULMAN, both British Subjects, and both of Department of Colloid Science, The University, Cambridge, Cambridgeshire, do hereby declare the nature of this invention to be as follows:—

This invention relates to toxicological preparations (by which expression we mean a preparation containing an agent toxic or repellent to insects, bacteria, fungi or the like) which can be applied to surfaces in the form of a thin film.

Known preparations of this character fall into two distinct categories. Those in the first form a film substantially impermeable to the toxic agent with the result that, although the preparation is extremely durable, the toxic agent is immobilised by the physical characteristics of the film and is so unable to exert its full toxic effect. With those in the second category the film is permeable to the toxic agent with the result that the toxic agent becomes rapidly exhausted.

The object of the invention is to provide a toxicological preparation of the above character which is durable but in which the film is sufficiently permeable to permit of adequate replenishment of the toxic agent at the surface of the film. The invention accordingly provides a toxicological preparation which can be applied to form a durable and tenacious film which contains a toxic agent uniformly distributed throughout a film-forming carrier mass, containing a liquid, which maintains an equilibrium between the carrier and the toxic agent such that, when the film is formed, the toxic agent will be free to travel to the surface at a controlled rate. In this way we obtain a preparation which will exercise a pronounced toxic action substantially unchanged for a prolonged period.

The carrier may consist of a suitable solid material previously impregnated with the toxic agent, which material can be converted into a gel by the addition of a liquid. Thus we may use silica dust converted into a gel by addition of water.

In the case where a toxic agent is insoluble or sparingly soluble in hydrophilic solvents, such as for example a gum and containing a proportion of the hydrophilic solvent and having uniformly distributed through it a solution of the toxic agent in a hydrophobic solvent. The solvent should be relatively non-volatile and in the case of pyrethrins may be constituted by a heavy oil of the medicinal paraffin type. In the case where the toxic agent is soluble in hydrophilic solvents the carrier will be a material insoluble in hydrophilic solvents, the toxic agent will be dissolved in a hydrophilic solvent and the preparation will contain a hydrophobic solvent in which the carrier is soluble.

In some of the preferred compositions, pyrethrins constitute the toxic agent and a dispersion of oil (e.g. a heavy oil such as the medicinal paraffin type) in a hydrophilic gel (e.g. chondrous jelly, or gum tragacanth) constitutes the carrier.

The storage capacity of the bulk carrier for pyrethrins depends on the relative proportions of the oil and water phases present, since pyrethrins are readily soluble in oil, but are almost insoluble in water. When the oil phase is dispersed by means of an emulsifying agent through the gel carrier, a mosaic or network of internal oil/water interfaces is produced through which the capillary active pyrethrins may readily penetrate. In a particular system the permeability of the carrier may be modified by alterations in the nature of the oil phase and by the incorporation of a hygroscopic agent (e.g. glycerine or calcium chloride) since the permeability of the films produced also depends on the viscosities of the oil and water phases. By these means the rate at which the pyrethrins become available at the outer surface of the repellent film may be adjusted as desired. The storage capacity and the availability of the pyrethrins may also be modified by the incorporation of finely divided powder or dust in the bulk carrier.

It will be appreciated that preparations of the above type are of the contact repellent type, but modifications may also comprise a composite type where a volatile repellent is present, so that joint contact and fumigant repellent action takes place.

The following composition is an example of a repellent cream according to the invention:—

Pyrethrins - - -	0.5%
Soft paraffin - - -	1%
Heavy oil - - - -	24%
Cetyl alcohol - - -	0.25%
Sodium cetyl sulphate -	0.4%

Chondrus jelly	3.5%
Calcium chloride	0.7%
Water	69.65%

This cream produces durable protective films when spread on the skin. Laboratory tests have shown that increase in the calcium chloride content increases the degree of repellent action. With the above composition films still show repellent action after 6—8 hours to flying insects such as Musca domestica, Phormia terra-novae, and to crawling insects such as Tenebrio adults and larvae. The proportion of calcium chloride or similar hygroscopic agent desirable depends on the particular gum or gel component used. In the above preferred composition, only a small proportion of calcium chloride is necessary owing to the relative hygroscopicity of the chondrus jelly.

Dated this 22nd day of January, 1943.

BREWER & SON,
Chartered Patent Agents,
33, Chancery Lane, London, W.C.2.

COMPLETE SPECIFICATION

Improvements in or relating to Toxicological Preparations

We, HARRY HURST and JACK HENRY SCHULMAN, both British Subjects, and both of Department of Colloid Science, The University, Cambridge, Cambridgeshire, and STAFFORD ALLEN AND SONS LIMITED, a British Company of Wharf Road, London, N.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The object of this invention is to provide insecticidal preparations having a greater toxicity, for a given content of insecticide, than the insecticidal preparations at present available.

Broadly stated, the invention consists in an insecticidal preparation comprising a stable disperse system of water and a non-volatile mineral oil, wherein water constitutes the overall continuous phase, an added organic insecticide dissolved in the oil phase, a hygroscopic agent and a dispersing agent having the property of stabilising the oil/water interfaces of the system and ensuring persistence thereof after application of the preparation to a surface or as a spray.

By the expression "stable" we mean that the disperse system will not readily break when applied to a surface to be freed from or rendered untenable by parasites, or when sprayed in the form of a mist. This persistence of the disperse system, which is achieved by the use of a dispersing-agent having the above-mentioned properties, is an essential and distinctive characteristic of preparations according to the invention. The oil is sufficiently non-volatile to prevent it from evaporating with undue rapidity, and the presence of the hygroscopic agent will prevent undue loss of the aqueous phase by evaporation.

As will be noted below, the preparations according to the invention may consist of emulsions, in which case the required stability of the interfaces can only be produced by using a composite emulsifying agent comprising an oil-soluble long chain organic compound and a water-soluble long chain organic compound. The preparations may however, be thickened to form creams, which can spread on the skin to form a protective film. In this case the dispersing agent employed for stabilising the interfaces can be a single dispersing agent which will be concentrated by adsorption at the interfaces.

Our researches have shown that for insecticides to be effective against parasites a certain threshold concentration is required. Owing to the fact that the insecticide is concentrated in the disperse phase of the preparation, the quantity of insecticide per unit volume of the preparation as a whole required to produce the threshold concentration of toxicant will be considerably less than would be needed if the toxicant were employed in solution in a single bulk liquid phase. Where, moreover, the insecticide is capillary active, a still smaller quantity of insecticide per unit volume of the preparation will be effective to produce the threshold concentration owing to the further concentration of the insecticide at the oil-water interfaces of the system.

Insecticidal preparations consisting of a kerosene solution of pyrethrins emulsified in water are of course known. The water has, however, hitherto been considered merely as a convenient vehicle for facilitating the spraying of the preparation and it has been thought desirable to provide for rapid break-down of the emulsion, after application, to get rid of the water and form an oil film on the treated surface. It has not hitherto been realised that it is possible to employ, in such emulsions, a greatly reduced content of pyrethrins, for a given toxic effect, than is needed with a kerosene solution

pure and simple. Nor has it been appreciated that the effectiveness of such an emulsion with a reduced pyrethrin content depends (a) upon the use of a dispersing agent which will stabilise the oil/water interfaces and (b) upon the preservation of the oil/water interfaces (and also of the water/air interfaces at which the pyrethrins may also be concentrated) during and after application by incorporation of a hygroscopic agent in the emulsion. Insecticidal preparations are applied, usually by spraying, either to form a toxic mist or a thin film on the surface to be freed from insects and it will be understood that, unless a hygroscopic agent is included the oil/water and water/air interfaces will rapidly disappear owing to evaporation of the water. Where water is present, the pyrethrins may spread far more rapidly over the cuticle of an insect than they can in the presence of oil alone and are therefore more easily able to exert a toxic action.

The insecticide will be an organic body added to the oil phase, as distinct from constituting an impurity therein, and may be either naturally occurring, such as pyrethrins (which is the preferred example), rotenone or nicotine, or synthetic, such as the material sold under the Registered Trade Mark "Lethane" which is said to consist of a mixture of alkyl isothiocyanates. Other toxicants in addition to the insecticide, however, may be incorporated in suspension or solution in either component of the disperse system to improve the efficiency of the spray where additional or special adjuvant action is desired, e.g. fungicidal spray materials such as copper, mercury, or sulphur compounds, or substances such as derris or cubé, or arsenic derivatives, or similar substances which act as stomach poisons.

We prefer to use kerosene for the oil phase in the case of emulsions to be used as fly sprays. For warehouse sprays a heavier oil, e.g. an oil of the medicinal paraffin type or Shell Oil P 31 is usually employed. Solvents such as tetralin, dekalin, oil of sesame, Ceylon citronella oil, benzyl benzoate, cyclohexanone or methyl cyclohexanol may be incorporated in the oil phase. The expression "non-volatile mineral oil" as used herein does not include creosote and like tar oils.

An insecticidal spray composition has been proposed, which consists of an emulsion in water of liquid aliphatic mono-olefine hydrocarbons boiling below 600° F. (which may be mixed with petroleum derived spray oils), and which contains as the emulsifying agent partially hydrolyzed esters of glycerol, it being stated that the emulsion may be employed in conjunction with extracts of rotenone, pyrethrum and the like. This emulsifying agent would not, however, stabilise the oil/water interfaces of the system.

According to another prior proposal, an emulsion of creosote oil and a vegetable or animal non-drying oil, which may contain pyrethrins and also glue or gelatine as a stabilising agent and calcium chloride as a hygroscopic agent, is employed as an insecticide. This proposal is differentiated from our invention by virtue of the nature of the oil phase, and also by the absence of the feature of stabilised oil/water interfaces.

Another earlier proposal is an insecticide comprising an aqueous solution containing a hygroscopic agent and charged with sulphur dioxide, it being stated that part of the water may be replaced by an oil such as an animal oil and an emulsifying agent incorporated. This preparation did not, however, include an organic insecticide, nor was there any suggestion of stabilising the oil/water interfaces.

Finally, in Specification No. 462,051 there is described an insecticidal oil spray emulsion, containing a mineral oil in which is dissolved a tetra-alkylthiuram monosulphide and an emulsifying agent consisting of casein and a base such as triethanolamine, butylamine, ethylamine, amylamine or the like. This type of composite emulsifying agent will not, however, operate to stabilise the oil/water interfaces of the system.

A hygroscopic agent is, as explained above, an essential constituent of preparations according to the invention. This will be present in relatively small proportions, usually not exceeding 5% by weight of the preparation as applied. Where however the preparation is put up in the form of a concentrate to be diluted for use, the proportion of hygroscopic agent in the concentrate will naturally be higher.

Insecticide preparations according to the invention include the following types:—

(1) Oil in water emulsions.
(2) Creams.

Now taking pyrethrins as an example of a typical insecticide, in the case of oil in water emulsions, adjuvant action is obtained both from the oil phase, the water phase, and the interfaces between the two phases of the emulsion.

Pyrethrins are relatively insoluble in water, and so far as the water is concerned adjuvant action depends mainly on the high concentration of pyrethrins adsorbed at the air/water interfaces. Pyrethrins

are readily soluble in oils such as kerosene, and the kerosene exercises an adjuvant action firstly because of the high local concentration of pyrethrins due to the dispersion of the oil throughout the system in fine droplets and secondly because kerosene and like oils act on the cuticle of an insect to increase its permeability and hence the susceptibility of the nervous system of the insect to the pyrethrins. A further and more important adjuvant action arises from the concentration of the pyrethrins by adsorption at the oil/water interfaces of the system.

We find that pyrethrins, being capillary active, spread very rapidly at water/air and oil/water interfaces, due to the high concentration of pyrethrins established at these interfaces by adsorption. On the other hand pyrethrins spread very slowly over an oil/air interface because there is no marked lowering of the surface tension at the interface. Where the pyrethrins are simply dissolved in a bulk oil carrier, spreading of the pyrethrins takes place slowly and depends on solution and diffusion through the bulk oil phase.

Warehouse sprays, which are commonly applied atomised to form a thin film on walls and other surfaces to free them from insects, generally consist of a solution of pyrethrins in a heavy oil. In practice the toxic effect disappears rapidly mainly owing to the passage of the pyrethrins into pores in the surface, and it is necessary to have recourse to repeated applications of the material in order to maintain a toxic film.

Warehouse sprays according to the invention however will, when the oil/water ratio in the emulsion is fairly high, form a persistent viscous film on the treated surface; because when the emulsion is sprayed on a porous surface, such as wood or paper, the surface will imbibe part of the water. This reduction in the water content of the film increases the viscosity of the emulsion, and reduces the tendency of the insecticide to penetrate into the pores of the surface.

Insecticidal preparations according to the invention may also be put up in the form of a cream, to be applied as a protective film to the skin for the purpose of keeping parasites at a distance. To this end the disperse system is rendered viscous by the incorporation of a suitable thickening agent, as hereinafter explained in greater detail.

Insecticidal creams as at present in use fall into distinct categories. Those in the first employ a gum as carrier for the insecticide, and form a film which is substantially impermeable to the insecticide, with the result that, although the preparation is extremely durable, the insecticide is immobilized by the physical characteristics of the film and is so unable to exert its full toxic effect. In those in a second category, a carrier of the hard or soft paraffin or cold cream type is employed and the film is easily wiped away and is permeable to the insecticide to such an extent that the insecticide becomes rapidly exhausted. Those of the vanishing cream type are absorbed by the skin, rendering the insecticide immobile.

Insecticidal creams according to the invention however constitute a desirable compromise between these extremes. The preparation, when applied, forms a durable and tenacious film, but the insecticide is free to travel to the surface of the film at a controlled rate such that the preparation will exercise a pronounced toxic action substantially unchanged for a prolonged period.

The following is a more detailed description of certain specific insecticidal preparations according to the invention:

1. Emulsions (Type A) Suitable for Use Against Flying Insects.

These are made by incorporating pyrethrins in an oil in water emulsion, but may contain in addition secondary toxicants such as rotenone, isobutylundecylenamide (which is sold in the Trade as IN 930), Thanite (the Trade name of a material stated to be fenchyl thiocyano acetate), mixtures of rhodanates or thiocyanates or citronella oil.

It is preferred to use a light mineral oil such as kerosene and a hygroscopic agent such as glycerine or chondrus jelly dissolved in the water phase. The emulsifying agent consists of an oil soluble component, such as cholesterol, cetyl alcohol, oleyl alcohol, or a commercial preparation of mixed secondary alcohols (e.g. C 10—C 18) or geranium oils, or other commercial oil soluble alcohols, or amines or essential oils containing alcohols, and a water soluble component, e.g. a neutral soap such as sodium cetyl sulphate, sodium oleyl sulphate or hexadecyl trimethyl ammonium bromide.

Where a composite emulsifying agent is used, a molecular complex of two substances, one oil soluble and the other water soluble, is present at the interfacial film. We find that a higher rate of knock-down of flying insects is obtained when the molecular complex is liquid than when it is solid. Liquid complexes are obtained when the oil soluble component of the emulsifying agent is cholesterol oleyl alcohol, geraniol or a

secondary alcohol within the range C10—C18. Solid complexes are frequently obtained when the oil soluble component is cetyl alcohol.

Emulsions of this type produce a rapid knock-down effect on flying insects when applied as a fine spray. In addition, when the emulsion contains a relatively high proportion of oil, e.g. 35% by volume or more, surfaces which have been sprayed show a pronounced repellent action to insects which subsequently settle on them. This is due to the fact that, as previously explained with reference to warehouse sprays, a relatively large increase in viscosity of the emulsion may be produced by a small reduction in the proportion of water phase present. This occurs when the emulsion is sprayed on a porous surface such as wood, or paper which imbibes part of the water in the sprayed droplets. As a result the bulk of the spray droplets remain immobilized on the outer surfaces of porous materials, and are therefore available for toxic action for some time after the spray has been applied. Where the carrier consists of a mineral oil alone, as for example in fly sprays in general use, the bulk of the spray is rapidly absorbed by porous surfaces shortly after application and becomes no longer available for toxic action. This persistent toxic action depending on the formation of a viscous toxic film of emulsion is unattainable with fly sprays of the pyrethrum mineral oil type in general use.

Our researches have shown that water is an adjuvant for contact nerve poisons such as pyrethrins in emulsion carriers. This adjuvant action is most pronounced when the emulsion carriers are stable, for it depends on the maintenance of the oil-water interfaces in the emulsion spray after application. Relatively high concentrations of a capillary active toxicant such as pyrethrins are present at these interfaces. When the water is removed or allowed to evaporate, pyrethrins will remain uniformly distributed in the bulk oil phase which remains. Research has shown that when this occurs, there is a pronounced drop in the toxity of the insecticidal film, owing to the fact that local high concentrations of pyrethrins are no longer present when the water phase of the emulsion carrier is absent. When water is reintroduced into the film, there is an increase in toxicity.

Stability is an essential characteristic of emulsions according to the present invention, in which the water phase is an essential component. The presence of a hygroscopic agent, such as glycerine, glycols or chondrus jelly, in small proportions assures the preservation of the water phase in the film.

The emulsion may, if desired, be put on the market in the form of a concentrate to be re-emulsified with oil and water before application.

2. EMULSIONS (TYPE B) GENERAL PURPOSE CONCENTRATE SUITABLE FOR DILUTION WITH WATER.

Research has shown that flying insects such as house-flies, mosquitos, are relatively susceptible to a mist of atomised light mineral oil such as kerosene, but this effect is much less pronounced with crawling insects such as beetles, beetle larvae, butterfly and moth larvae, bed bugs and plant bugs.

The conditions under which these insects occur make it undesirable to use a spray containing a high oil content, because the oil may damage the surface to which the emulsion is applied. Thus it may stain the surface and, in the case of painted surfaces, dissolved the paint. Also many plants harbouring insect pests are damaged by too high a concentration of oil in the emulsion.

Emulsions of the kind described for use against flying insects (i.e. Type A emulsions) produce a rapid knock-down effect, even with a very low content of pyrethrins, because of the effect on the insects of the relatively high proportion of oil. When diluted with water, emulsions are not very effective against flying insects, because a sprayed mist no longer persists due to the high water/oil ratio. Such dilute emulsions require to have a much higher concentration of pyrethrins in the oil phase and are then very effective against crawling insects, since much larger dosages can, owing to the dilution, be applied with an adequate factor of safety to surfaces to be freed from such insects than would be possible with the more concentrated emulsions.

Emulsions of this type therefore may take the form of a concentrate similar to that suitable for use against flying insects but containing up to 100 times as much pyrethrins, which may be diluted with large volumes of water, e.g. from 10 to 1000 volumes of water before application.

In the case of emulsions to be diluted before application we may with advantage employ, as an alternative to kerosene, higher boiling paraffins of the medicinal paraffin type or mixtures containing a proportion of the higher boiling components known as soft or hard paraffins.

It has been shown for example that the lower boiling mineral oils, such as kerosene, produce a more rapid insecticidal action than the higher boiling

mineral oils, but these latter have a more prolonged action since they persist in the sprayed film for a longer period than the more volatile lower-boiling oils, and in certain conditions are desirable, e.g. on surfaces where the lower-boiling oil would prove harmful.

The emulsifying agent, as in the case of Type A emulsions, consists of a mixture of an oil-soluble and of a water-soluble component the proportions of which are adjusted to give a stable emulsion at the dilution desired for practical spraying.

The emulsion may be put on the market in the form of a concentrate to be diluted with large volumes of water before application.

As before, the water phase will contain a hygroscopic agent, e.g. glycerine, glycols or chondrus jelly or gum, which has the property of attracting, water, which may act as a thickening agent or as a " spreader " or " sticker " to prolong the duration of the insecticidal film. Gums, such as tragacanth, which do not attract water are not included by the expression " hygroscopic agent."

Type B concentrates may be diluted with water or with an aqueous solution of a stabilizer (e.g. gelatin or gum, which also act as stickers) or of a spreader (e.g. soap).

3. Warehouse Sprays.

These consist of an emulsion in water of a heavy oil of the medicinal paraffin type containing pyrethrins or other suitable insecticide in the disperse phase and having a high oil/water ratio. As already explained this assures the formation of a persistent insecticidal film. The material includes a hygroscopic agent, e.g. glycerine, glycols or suitable water-attracting gum, such as pectin, which will ensure the presence of water in the disperse phase.

The preparations herein referred to as " warehouse sprays " are suitable not only for use in warehouses, but also for other applications, e.g. for impregnating fabrics, or treating surfaces or the coats of animals to which it is desired to apply an insecticidal or repellent film.

4. Insecticidal Creams.

In the creams according to the invention, the disperse system is rendered sufficiently viscous for the preparation to form a durable tenacious film when applied to the skin. This may conveniently be achieved by incorporating a gum in the water phase, e.g. gum tragacanth or chondrus jelly. Alternatively the water phase may consist of silica gel. As a further alternative soft or hard paraffins may be incorporated in the oil phase. Again the dispersion may be rendered viscous by the use of a solid dispersing agent such as hydrated alumina (preferably that sold under the Registered Trade Mark " Unemul "), or by the incorporation therein of a cellulose ester or a soap.

Repellent action is influenced mainly by the viscosity of the oil phase, the degree of intensity of repellency decreasing with increase in viscosity. Increase in the viscosity of the water phase produces little change in the degree of repellent action. It has been shown that the permeation of capillary active insecticides through dispersions of this type is influenced mainly by the viscosity of the oil phase and by the viscosities of the interfacial films formed at the oil-water interfaces of the system. The rate of permeation of insecticide decreases with increase in the above viscosities. The quantities of thickening agents embodied in the preparation will of course be adjusted to control the rate of travel of the insecticide through the film in such a way as to ensure persistence of its toxicity, while nevertheless permitting of satisfactory replenishment of insecticide removed when the surface of the film is rubbed off.

The preparation may include a dispersing agent of the composite type already mentioned including an oil-soluble and a water-soluble component. In the case of creams, the required stability of the interfaces can however be obtained by the use of a dispersing agent of the single type, which will be concentrated by adsorption at the interfaces, such as diglycol stearate or glyceryl mono-stearate, or a solid material such as hydrated alumina or a mixture of such materials.

The hygroscopic agent may conveniently be glycerine or diethylene glycol. This regulates the permeability of the film and hence the availability of the insecticide after application. For example, when a solid dispersing agent such as hydrated alumina is present, the availability of pyrethrins in the film increases when such a hygroscopic agent is present owing to displacement of adsorbed insecticide from the solid interfacial films. The degree of this displacement depends on the relative proportion of water present in the carrier mass. Again, when relatively large proportions of gum are present in the water phase a lage proportion of the insecticide may, in the absence of a hygroscopic agent, be immobilized in the bulk framework of the repellent film shortly after application. The presence of a hygroscopic agent however regulates the permeability of the

film and hence the availability of the insecticide. The storage capacity of the carrier mass for the insecticide may also be regulated by the incorporation of finely divided powder in the bulk carrier. When chondrus jelly is employed as the thickening agent this may, in some cases, act as the hygroscopic agent as well.

Creams of this nature may embody materials such as pyrethrins, oil of citronella or dimethyl phthalate, indalone or mixtures of these.

The following are specific examples of various types of insecticidal preparations according to the invention.

In these examples, the following materials are Registered Trade Marks:—

Teepol (which is a mixture of long chain alkyl sulphates), Lissolamine (which is a salt of a long chain quaternary ammonium compound), Unemul, Lethone, and Manucol (which is a processed alginate). Crystox is the Trade name for a material stated to be a glycol ether of pinene.

Type A Emulsions.

I.

Kersosene extract of pyrethrum containing 0.1% w/v pyrethrins (i.e. 0.1 gm. pyrethrins per 100 cc). 115 parts by volume
(Stabilized as described in Specification No. 547,927)

Rotenone - - - - -	0.05 parts by weight
Cyclohexanone - - -	1 part by volume
Oleyl alcohol - - - -	1 part by volume
Kerosene - - - - - -	240 parts by volume
Shell Oil P 31 - - - -	3 parts by volume
Chondrus extract - - -	0.1125 parts by weight
Teepol - - - - - -	11.25 parts by volume
Water - - - - - -	198 parts by volume
Hydroquinone - - -	0.03 parts by weight

II.

Kerosene extract as in I -	100 parts by volume
Rotenone - - - - -	0.05 part by weight
Cyclohexanone - - -	1 part by volume
Cholesterol - - - -	0.375 part by weight
Kerosene - - - - - -	380 parts by volume
Shell Oil P 31 - - - -	3.8 parts by volume
Lissolamine C - - - -	7 parts by weight
Chondrus - - - - -	0.1 part by weight
Hydroquinone - - - -	0.02 part by weight
Water - - - - - -	191 parts by volume

III.

As I but water 193 parts by volume, and
Ethylene glycol 5 parts by volume substituted for the Chondrus extract.

IV.

Kerosene extract as in I -	57.5 parts by volume
Rotenone - - - - -	0.05 part by weight
Cyclohexanone - - -	1 part by volume
Higher secondary alcohols C_{10}—C_{18} - - - -	1 part by volume
Oil of Sesame - - - -	11.4 parts by volume
Shell Oil P 31 - - - -	2.24 parts by volume
Chondrus extract - - -	0.1125 part by weight
Water - - - - - -	198 parts by volume
Teepol - - - - - -	11.25 parts by volume
Hydroquinone - - - -	0.03 part by weight
Kerosene - - - - -	286.5 parts by volume

V.

Kerosene extract as in I	115 parts by volume
Higher secondary alcohols C_{10}—C_{18}	1 part by volume
I.N. 930	22.8 parts by volume
Shell Oil P 31	2.24 parts by volume
Kerosene	217 parts by volume
Lissolamine C	6 parts by weight
Chondrus	0.1125 part by weight
Water	204 parts by volume
Hydroquinone	0.03 part by weight

VI.

Kerosene extract as in I	60 parts by volume
Cetyl alcohol	0.5 part by weight
Kerosene	140 parts by volume
Ceylon citronella oil	9 parts by volume
Teepol	5 parts by volume
Tragacanth	0.15 part by weight
Hydroquinone	0.01 part by weight
Water	95 parts by volume
Glycerin	0.1 part by weight

TYPE B EMULSIONS, CONCENTRATES FOR DILUTION WITH WATER.

No. 1.

Kerosene extract of pyrethrum containing 6.5% w/v pyrethrins (prepared as described in Specification No. 493,074 and stabilized as described in Specification No. 547,927)	60 parts by volume
Rotenone	0.208 part by weight
Methyl cyclohexanol	1.312 parts by weight
Benzyl benzoate	0.544 part by weight
Cyclohexanone	2.436 parts by weight
Cetyl alcohol	0.66 part by weight
P.31 Oil	1.2 parts by weight
Kerosene	55 parts by volume
Teepol	7 parts by volume
Chondrus extract	0.07 part by weight
Hydroquinone	0.01 part by weight
Water	56 parts by volume

No. 2.

Kerosene extract as in No. 1 and stabilized as described in Specification No. 547,927	40 parts by volume
Crystox	35 parts by weight
Dekalin	24 parts by volume
Ceylon citronella oil	1 part by volume
Lissolamine C	3.3 parts by weight
Chondrus	0.1 part by weight
Water	90 parts by volume

EMULSIONS SUITABLE FOR WAREHOUSE SPRAYS.

No. 1.

Kerosene extract of pyrethrum containing 6.5 w/v pyrethrins	6 parts by volume
Rotenone	0.033 part by weight
Cyclohexanone	0.6 part by volume
Alcohols C_{10}—C_{18}	0.66 part by volume
P.31	114 parts by volume
Teepol	7 parts by volume
Gelatine	0.05 part by weight
Chondrus extract	0.14 part by weight
Water	63 parts by volume
Calcium sulphate	1.0 part by weight

No. 2.

P.31 Shell Oil extract of pyrethrum containing 6.5 w/v pyrethrins	6 parts by volume
I.N.930	2 parts by weight
Cetyl alcohol	1 part by volume
P.31 Oil	128 parts by volume
Teepol	7 parts by volume
Chondrus	0.17 part by volume
Unemul	1.4 parts by weight
Water	50 parts by volume

No. 3.

P.31 Shell Oil extract of pyrethrum containing 6.5% w/v pyrethrins	6 parts by volume
Cyclohexanone	0.7 part by weight
Rotenone	0.05 part by weight
Crystox	1.4 parts by weight
Cholesterol	0.8 part by weight
P.31 Oil	110 parts by volume
Teepol	7 parts by volume
Chondrus	0.2 part by weight
Pectin	0.5 part by weight
Lissolamine	1.4 parts by weight
Water	80 parts by volume

INSECTICIDAL CREAMS.

CREAM I.

	Parts by weight
Hard paraffin	0.5
Soft paraffin	1.5
Purified Kerosene	2.5
Heavy mineral Oil P.31	10.4
Antioxidant (Specification 547,927)	0.1
Extract of pyrethrins according to Specification No. 493,074 containing 40% by weight pyrethrins	0.5
Unemul	52.0
Diglycol stearate	0.5
Chondrus solution (0.1% aqueous solution)	29.0
Glycerine	4.0
Hydroquinone	0.005
Pyrocatechol	0.005

CREAM II.

	Parts by weight
Soft paraffin	3.0
Heavy Oil P.31	10.0
Purified Kerosene	1.0
Citronella Java	4.0
Citronella Ceylon	3.5
Extract of pyrethrins as I	0.4
Unemul	56
Gum Tragacanth (0.2% aqueous solution)	31
Glycol	4.7
Hydroquinone	0.007
Sodium bisulphite	0.01

CREAM III.

	Parts by weight
Hard Paraffin	0.6
Soft paraffin	1.4
Heavy mineral oil P.31	4.6
Dimethyl phthalate	17.5
Unemul	49.0
Manucol (0.5% aqueous solution)	23.0
Carbitol	5.4
Hydroquinone	0.01

CREAM IV.

	Parts by weight
Shell Oil	10.0
Purified Kerosene	3.0
Dimethyl phthalate	8.6
Extract of pyrethrins as I	0.7
Unemul	53.0
Gum Tragacanth (0.5% aqueous solution)	5.0
Manucol (0.5% aqueous solution)	16.0
Dimethylene Glycol	4.0
Tannic acid	0.008

CREAM V.

	Parts by weight
Soft paraffin	1
Heavy Oil P.31	24
Extract of pyrethrins as I	0.65
Cetyl alcohol	0.25
Lissolamine	1.6
Chondrus Jelly (2.8% aqueous solution)	72
Hydroquinone	0.006

CREAM VI.

	Parts by weight
Hard paraffin	0.5
Soft paraffin	2.0
Heavy oil P.31	10.0
Purified Kerosene	1.0
Extract of pyrethrins as I	0.45
Dimethyl phthalate	9.5
Diglycol stearate	4.0
Gum Tragacanth (3.0% aqueous solution)	69.0
Glycerine	5.4
Pyrocatechol	0.01

CREAM VII.

	Parts by weight
Soft paraffin	3.2
Heavy oil P.31	5.4
Extract of pyrethrins as I	0.37
Citronella Java	5.4
Diglycol stearate	6.7
Unemul	5.8
Gum tragacanth (3.0% aqueous solution)	73.1
Glycerine	4.2
Pyrocatechol	0.005
Hydroquinone	0.003

In the foregoing examples, hydroquinone, pyrocatechol, sodium bisulphite and tannic acid are included as antioxidants; gelatine as a sticker; carbitol as an emollient; and dimethyl phthalate renders the creams repellent to insects.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An insecticidal preparation, comprising a stable disperse system of water and a non-volatile mineral oil, wherein water constitutes the overall continuous phase, an added organic insecticide dissolved in the oil phase, a hygroscopic agent and a dispersing agent having the property of stabilising the oil/water interfaces of the system and ensuring persistence thereof after application of the preparation to a surface or as a spray.

2. An insecticidal preparation comprising a stable emulsion in water of a non-volatile mineral oil, an added organic insecticide dissolved in the oil phase, a hygroscopic agent, and a composite emulsifying agent comprising an oil-soluble long chain organic compound and a water-soluble long chain organic compound.

3. An insecticidal cream, comprising a stable disperse system of water and a non-volatile mineral oil, the water constituting the overall continuous phase, a hygroscopic agent and an added organic insecticide dissolved in the oil phase, the system being sufficiently viscous to enable the cream to be spread to form a durable and tenacious film and including a dispersing agent having the property of stabilising the oil/water interfaces of the system, and ensuring persistence thereof after formation of said film.

4. An insecticidal preparation as claimed in any of the preceding Claims, in which the hygroscopic agent consists of glycerine, chondrus jelly or diethylene glycol.

5. An insecticidal preparation as claimed in any of the preceding Claims, in which the insecticide is an extract of pyrethrum flowers.

6. An insecticidal preparation as claimed in any of the preceding claims, in which the oil is kerosene.

7. An insecticidal cream as claimed in Claim 3, in which the thickening agent for rendering it viscous comprises a gum, silica gel, a soft or hard paraffin, or a solid dispersing agent such as hydrated alumina.

8. An insecticidal preparation as claimed in Claim 5, containing additional toxicants, e.g. rotenone, copper, mercury or sulphur compounds, or arsenic derivatives.

9. Insecticidal preparations substantially as described herein with reference to the foregoing examples.

Dated this 18th day of March, 1943.

BREWER & SON,
Chartered Patent Agents,
33, Chancery Lane, London, W.C.2.

Printed for His Majesty's Stationery Office, by M.M.P. Ltd.—1948